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METALLIC MEMBER HAVING THERMAL FATIGUE RESISTANCE AND METHOD FOR MANUFACTURING SAME

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Specification

1. Title

METALLIC MEMBER HAVING THERMAL FATIGUE RESISTANCE AND METHOD FOR MANUFACTURNG SAME

2. Claims

1. A metallic member with thermal fatigue resistance having a diffusion coating layer of metal on the surface thereof, characterized in that a fine recrystallized grain layer is formed on the outermost surface layer of said diffusion coating layer.

2. The metallic member with thermal fatigue resistance of claim 1, wherein said metallic member is a nickel-based alloy, cobalt-based alloy, or iron-based alloy.

3. The metallic member with thermal fatigue resistance of claim 1 or 2, wherein said diffusion coating layer is a diffusion coating layer of Al or Cr.

4. The metallic member with thermal fatigue resistance of claim 1 or 2, wherein said diffusion coating layer is a compound diffusion coating layer comprising a second element in addition to Al or Cr.

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[1] Numbers in the margin indicate pagination in the foreign text.

5. A method for manufacturing a metallic member having thermal fatigue resistance characterized by:

subjecting the surface of a metallic member having a metal diffusion coating layer to plastic deformation, and

heating to a temperature above the recrystallization temperature to form a fine recrystallized grain layer on the outermost surface of said diffusion coating layer.

6. The method for manufacturing a metallic member having thermal fatigue resistance of claim 5, further characterized in that said metallic member is comprised of a nickel-based alloy, cobalt-based alloy, or iron-based alloy.

7. The method for manufacturing a metallic member having thermal fatigue resistance of claim 5 or 6 wherein said diffusion coating layer is an Al or Cr diffusion coating layer.

8. The method for manufacturing a metallic member having thermal fatigue resistance of claim 5 or 6 wherein said diffusion coating layer is a compound diffusion coating layer comprising a second element in addition to Al or Cr.

3. Detailed Description of the Invention

(Industrial Field of Application)

The present invention relates to metallic members having thermal fatigue resistance, and more particularly, to metallic members useful as coated rotor and stator blades, such as the

blades and nozzles employed in gas turbines, and to a method for manufacturing the same.

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(Prior Art)

Rotor and stator blades manufactured by precision casting from nickel-based or cobalt-based alloys are generally employed in gas turbines. In particular, nickel-based alloys with good high-temperature strength are employed in rotor blades. Although nickel-based alloys afford good high-temperature strength, they have a problem in the form of poor high temperature corrosion resistance. Improving corrosion resistance requires the application of a coating. The various methods of applying coatings include: diffusion, vapor deposition, thermal spraying, and combinations of the same. Surface treatment coatings applied by these methods must remain stable for extended periods in the face of high thermal stress and high-temperature corrosion. The most generally employed method is an Al diffusion coating. The crystal grains in coating layers formed by this treatment are large. When employed in the rotor blade of a gas turbine, cracks due to thermal stress accompanying plant starts and stops form in the surface of the coating. When the cracks increase in size, holes form, corrosive gas enters, and the base material corrodes.

(Problem to Be Solved by the Invention)

The coating layers obtained by conventional coating treatments do not take resistance to thermal fatigue into account, and are problematic in that they develop cracks when subjected to high levels of thermal stress. The crystal grains in the coating layer are large and cracks generally develop along the boundaries of the grains. When the cracks are of a length that reaches the base material, corrosive gas reacts with the base material, corroding the base material and extending the cracks. As a result, the function of a coating imparting resistant to corrosiveness is compromised.

The object of the present invention is to provide a metallic member and a treatment method that enhance the resistance to thermal fatigue of the surface of a coating layer obtained by known coating treatments.

(Means of Solving the Problem)

To summarize the present invention, the first invention relates to a metallic member with thermal fatigue resistance having a diffusion coating layer of metal on the surface thereof, characterized in that a fine recrystallized grain layer is formed on the outermost surface layer of said diffusion coating layer.

The second invention relates to a method for manufacturing a metallic member having thermal fatigue resistance characterized by: subjecting the surface of a metallic member having a metal diffusion coating layer to plastic deformation, and heating to a temperature above the recrystallization temperature to form a fine recrystallized grain layer on the outermost surface of said diffusion coating layer.

The present inventors discovered that forming fine crystal grains in the vicinity of the surface of the coating layer enhanced the resistance to thermal fatigue of the coating layer. To impart fine crystal grains, the coating layer surface is plastically deformed by shot peening and then heat treated to cause recrystallization. The recrystallization results in fine crystal grains. Fine crystal grains are known to have high yield strength, enhancing the resistance to thermal fatigue of the coating layer.

The rotor blades employed in gas turbines are generally manufactured by precision casting. Since they are corroded by corrosive substances such as Na_2SO_4 and NaCl contained in combustion gases, coating treatments are applied for surface protection. The coating treatment is generally in the form of an Al diffusion coating. When the base material is a nickel-based alloy, this coating layer forms the intermetallic compound NiAl,

and when the base material is a cobalt-based alloy, the intermetallic compound CoAl. These compounds protect the base material from corrosive gases and enhance the resistance to corrosion of the base material.

The stator blades employed in gas turbines are subjected to great thermal stress during repeated starting and stopping of the plant. This thermal stress generates cracks and causes cracks to develop on the coating layer surface during extended periods of use at high temperature. The cracks allow corrosive gas to pass through voids in the coating layer and cracks occurring along grain boundaries, damaging the base material.

The generation of cracks can be stopped by forming fine recrystallized grains in the coating layer.

The size of the crystal grains in the coating layer can be controlled by subjecting the coating layer surface to plastic deformation by shot peening, for example. Portions subjected to plastic deformation have high deformation energy, and when subsequently subjected to heat treatment, serve as the nuclei of new crystal grains. Recrystallization forms fine crystal grains in the coating layer.

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These fine crystal grains increase the yield strength of the coating layer, making it possible to obtain a coating layer

with good resistance to thermal fatigue without a loss in resistance to corrosion.

The relation between crystal grain size and the yield strength of a material is clear from the known pitch relation equation. The pitch relation equation is given below as Equation (1).

$$\sigma y=\sigma o + Ad^{-1/2} \qquad (1)$$

where σy: yield strength

σo, A: constants

d: crystal grain diameter

This equation shows that the smaller the crystal grain diameter, the greater the yield strength of the material.

Specific examples of applications of the member of the present invention are the blades and nozzles employed in gas turbines, such as coated rotor blades.

Fig. 3 shows a sectional configurational view of a gas turbine nozzle and Fig. 4 shows a sectional view along section line A-A in Fig. 3. In the figures, 1 denotes a retainer ring, 2 denotes a cooling air flow, 3 denotes a high-temperature combustion gas flow, 4 denotes a nozzle segment, and 5 denotes a coating layer.

(Embodiments)

The present invention is described in greater detail below through embodiments. However, the present invention is not limited to the embodiments.

Embodiment 1

A simulated blade precision cast from a nickel-based alloy of the composition shown in Table 1 was coated by the following method.

Table 1: Composition of nickel-based alloys (wt%)

Component	C	Cr	Mo	Fe	Co	Ti	Al	W
Analysis	0.12	15.74	1.76	0.21	8.29	3.25	3.26	2.60

Component	B	Zr	Si	Mn	Nb+Ta
Analysis	0.015	0.069	<0.01	0.01	2.56

The simulated blade was diffusion coated with Al under the following conditions. A mixed powder of 25 percent pure Al, 72.5 percent industrial Al_2O_3, and 2.5 percent NH_4Cl was employed as the packing agent. The blade was treated by being dipped in this powder and heated at a temperature of 750°C for 4 hours in an argon atmosphere. In the Al agent reaction, aluminum chloride was generated from the packing agent starting material and Al separated from the Al chloride on the surface of the blade being treated in the known manner. The Al diffused from the surface inward. Identification of the surface of the blade

that had been diffusion coated with Al by X-ray analysis confirmed that an Ni-Al alloy comprised chiefly of the intermetallic compound Ni_2Al_3 had formed.

Next, the blade was heated for two hours under a vacuum at 1,121°C and cooled to room temperature. Subsequently, the blade was heat treated for 24 hours in a vacuum at 843°C and cooled to room temperature. X-ray analysis of the diffusion coating layer identified NiAl.

The Al diffusion coated surface was subjected to five hours of shot peening to plastically deform the surface of the diffusion coating layer. The metallic member thus processed was then heat treated at 900°C for one hour.

Fig. 1-1 is an optical microscope photograph (400X magnification) of the texture of the metal in a cross-section of the coating layer that had been plastically deformed by shot peening, and Fig. 1-2 is an optical microscope photograph (400X magnification) of the texture of metal that had not been plastically deformed. A comparison of the photographs reveals that Fig. 1-1 has finer grains.

Embodiment 2

Al coating was conducted by chemical vapor deposition using a sample obtained by precision casting a simulated blade by the same method as in Embodiment 1. The chemical vapor deposition

was conducted for 30 minutes at a vacuum of 10 Torr and a processing temperature of 950°C. $AlCl_3$ was employed as carrier gas. The $AlCl_3$ decomposed on the base material and penetrated into the base material by Al diffusion. X-ray analysis of the Al diffusion coating layer identified the intermetallic compound NiAl.

Subsequently, the blade was solution heat treated for 2 hours at 1,121°C and subjected to an aging treatment for 24 hours at 843°C. Shot peening was conducted in the same manner as in Embodiment 1.

The graph of Fig. 2 shows the results of a thermal fatigue test indicating the number of heat cycles conducted before cracking appeared. The method employed in the thermal fatigue test was as follows: a sample measuring 20 x 50 x 5 mm in size was subjected to a heat cycle in which it was maintained at an elevated temperature of 900°C for 30 minutes, moved to a low-temperature vessel maintained at 300°C and kept there for 5 minutes, and then moved back to a high-temperature vessel at 900°C.

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The thermal fatigue resistance evaluation method consisted of determining the number of heat cycles required before cracks 1 mm in length appeared on the surface of the coating layer.

As indicated in Fig. 2, subjecting a coating layer to plastic deformation followed by recrystallization based on the present embodiment yielded a metallic member with a coating layer having good resistance to thermal fatigue.

(Effect of the Invention)

Since the present invention permits the formation of fine crystal grains in a coating layer, it is effective in the manufacturing of metallic members having thermal fatigue resistant coating layers. Even when cracks do appear, the small diameter of the grains has the effect of slowing down the rate of progression of the cracks and increasing the resistance of the coating layer to separation.

4. Brief Description of the Drawings

Fig. 1-1 is an optical microscope photograph of the texture of metal in the cross-section of a coating layer subjected to plastic deformation by shot peening. Fig. 1-2 is an optical microscope photograph of the texture of metal that was not subjected to plastic deformation. Fig. 2 is a graph showing the results of a thermal fatigue test showing the number of heat cycles conducted before cracks appeared. Fig. 3 shows a sectional configurational view of a gas turbine nozzle and Fig. 4 shows a sectional view along section line A-A in Fig. 3.

1: Retainer ring; 2: Cooling air flow; 3: High-temperature combustion gas flow; 4: nozzle segment; 5: Coating layer

[Fig. 2]

[(#left) No. of thermal cycles before cracking (#top) Did not crack (#below 350) Comparative material (coated) (#inside 1130, left) Embodiment 1 (#inside 1130, right) Embodiment 2 (#below 1130) Material of the invention]

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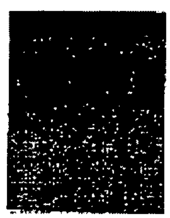
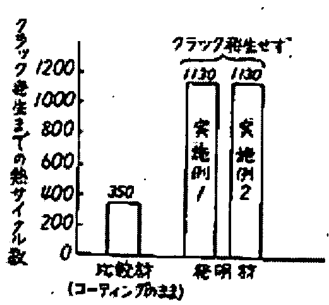
[Fig. 3]

[(3) Direction of high-temperature gas flow (#top center) Cooling air]

第1-1図

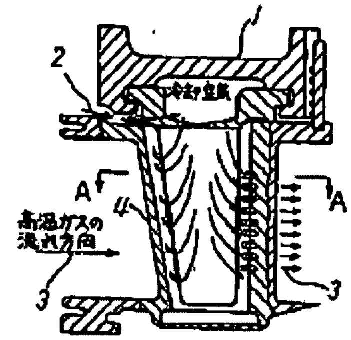


第1-2図



第2図

第 3 図



第 4 図